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Decomposition of zinc ferrite in zinc leaching residue by reduction roasting

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Abstract

A new method to decompose zinc ferrite ($ZnFe_2O_4$) in zinc leaching residue was developed in this paper. Zinc ferrite was decomposed to zinc oxide and magnetite after reduction roasting using the mixture of carbon monoxide (CO) and argon（Ar）as reduction agent. The phase transformation in reduction roasting of samples was determined by XRD, the effects of roasting temperature on the distribution of zinc and iron at different particle size were investigated by chemical analysis. And the acid leaching process was applied to evaluate the decomposition of zinc ferrite in different roasting conditions. The results suggest that the zinc ferrite in zinc leaching residue could be well decomposed in roasting process and the optimal roasting condition is 850°C, 2h.

Keywords: reduction roasting; zinc leachingresidue; zinc ferrite

1. Introduction

More than 85% of zinc is produced by zinc hydrometallurgical roast-leach-electrowinning processes all over the world. Iron-bearing sphalerite is a main raw material for this conventional process. Inevitably, spinels-oriented zinc ferrite is generated during the desulphurising roasting process of sphalerite[1]. Zinc ferrite is hardly soluble at mild sulphuric acid conditions because of its stable configuration [2, 3]. Consequently, zinc ferrite is always presented as a main component of zinc leaching residue [4], which is

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set aside and left as an unresolved problem [5]. Moreover, this residue is a hazardous waste because it contains large amounts of zinc and other heavy metals, such as Cu, Pb, Mn and Cd [6]. The concerns are not only environmental but economic, as well. The recycling of this residue as a resource instead of a waste is notably attractive because of the depletion of zinc ores and the rapid rise of metal prices [7].

Various hydrometallurgical and pyrometallurgical processes for decomposition of zinc ferrite were currently used. Hydrometallurgical processes such as two-stage acid leaching [8], high pressure acid leaching [9, 10], various acids leaching [11-13] microwave caustic leaching [14], and alkaline leaching [15] have been developed. In addition, several other hydrometallurgical processes, including the use of ammoniac solutions [16, 17] and chloride (FeCl3 and NaCl) leaching [18-20] are being conducted. High decomposition of zinc ferrite is achieved in those processes. However, they are unsuitable for the further treatment of roasting process for the iron and many other heavy metals are left in the Zn hydrometallurgical solution so that a lengthy purification process is required before electrowinning. Moreover, this purification process produces a considerable amount of iron slag, which is a significant threat to the environment. The sophisticated purification process and high environmental risk make these leaching processes unsuitable for mass production of zinc ferrite's decomposition. Pyrometallurgical methods are dominated by the Waelz process [21] and consist of transformational roasting processes, including Na2CO3 roasting [22-24] and sulphation roasting [7, 25], whereby zinc ferrite is converted into soluble zinc and iron compounds under high temperature. However, in the Waelz process, most of the irons contained in zinc ferrite is reduced into metallic iron and subsequently agglomerates into balls with other compositions of zinc-leached residue. The hardness of these balls makes them difficult to treat. For the transformation roasting processes, it is necessary to employ the same long purification processes following the extraction, as in hydrometallurgical processes.

This paper focuses on the decomposition of zinc ferrite in zinc leaching residueby a reduction roasting process. In this process, a mixture of carbon monoxide (CO) and argon (Ar) is applied as a reducing agent. The reactions during roasting process are as follows.

$$3\ ZnFe_2O_4 + CO = 3\ ZnO + 2\ Fe_3O_4 + CO_2 \quad (1)$$

$$ZnFe_2O_4 + CO = ZnO + 2FeO + CO_2 \quad (2)$$

By applying a weak reducing agent, generation of ferrous oxide and metallic iron, which result from traditional roasting processes using carbon as the reducing agent, can be avoided. Moreover, this process also has the advantages of a lower roasting temperature than the traditional process and a simple processing flow. In this study, the effect of the roasting temperature and the roasting duration on the decompositionof zinc ferritewas investigated. Meanwhile, the transformation of the phases and microstructure in reduction roasting was also involved.

2. Material and Methods

2.1. Materials

Materials The zinc leaching residue with 19.70% zinc and 23.91% iron, which was used in this study, was obtained from a zinc hydrometallurgical plant located in Zhuzhou, Hunan, China. The sample was sieved to obtain a different level of particle sizes and was dried at 105℃ for 5-6h. X-ray diffraction presented in Fig.1 showed that magnetite and zinc ferrite were the main mineral phases in zinc leaching residue and zinc sulphide, lead sulphate, zinc oxide and zinc silicate were detected as minor phases.

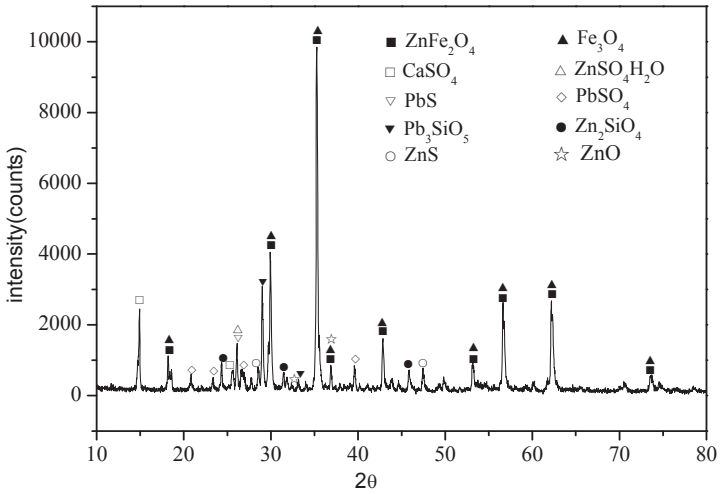


Figure 1 XRD of zinc leaching residue

2.2. Reduction roasting

The roasting process is conducted in a reduction roasting furnace. The samples are placed flatly in a crucible and heated under a nitrogen-rich atmosphere to a desired reduction temperature and carbon monoxide gas is later introduced for reduction. After a certain roasting duration, the reducing gas mixture of carbon monoxide and nitrogen is replaced by nitrogen, and the roasting product is cooled to room temperature in the furnace. Roasting temperatures ranging from 700℃ to 900℃at 50℃ increments and roasting duration ranging from 1h to 3.5h at 0.5h increments were examined, while volume fraction of CO was held constant at 10%.

2.3. Acid leaching process

During sulphuric acid leaching procedure, experiments were carried out using H2SO4 solution with an acidity of 150g/L. Leaching was performed at room temperature at the S/L of 15:1, under mechanical stirring (600rpm) for a time of 2h. The leaching residue was separated from the liquid phase by vacuum filtration, then washed with deionized water, and then dried at 105℃ for 6h and analysed.

2.4. Characterisations of samples

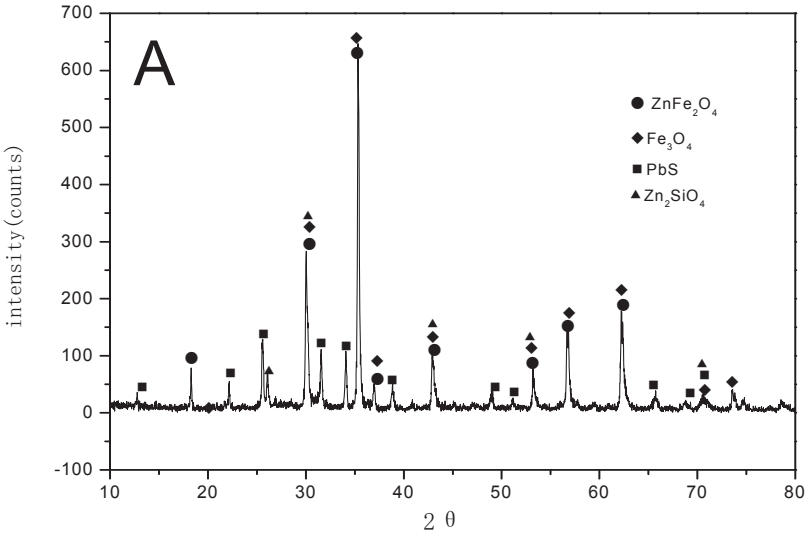
X-ray diffraction (XRD) analysis (Rigaku-TTR) is carried out to determine the phase of original sample and the transformation of the phases during the roasting process. Potassium dichromate titration for Fe and EDTA titration for Zn were used for the chemical analysis of samples.

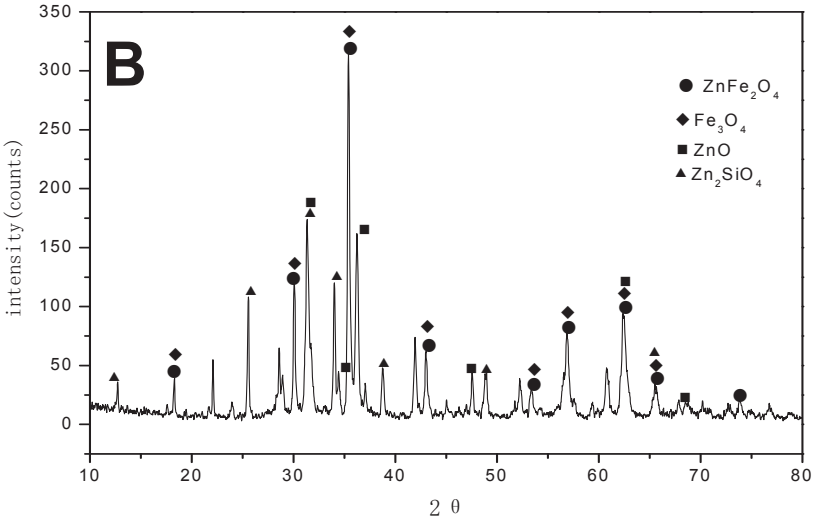
3. Results and Discussion

3.1 Results of XRD of different roasting temperature

XRD analyses were performed to find out the effect of roasting temperature on the decomposition of zinc ferrite when the duration of roasting and the volume fraction of CO were held constant at 2h and 10%, respectively, and the results are shown in Fig.2. It could be observed in Fig.2A that the main phases of zinc are zinc ferrite and zinc silicate, and the main phases of iron are zinc ferrite and magnetite; the level of decomposition of zinc ferrite is so low that zinc oxide couldn't be detected in roasting product. With the increase of temperature, as the Fig.2B and Fig.2C show, the contents of zinc ferrite, magnetite and zinc oxide in roasting product under 850 °C and 900°C are much more than 700°C, meanwhile, zinc ferrite, zinc silicate and zinc oxide are determined as the main phase of zinc and magnetite is the main phase of iron.

A comparison of the XRD patterns of original sample and the roasted samples reveals that the intensity of the characteristic peaks of zinc ferrite decreases with the increase of roasting temperature. It is also observed that the intensity of the characteristic peaks of zinc oxide in the roasting product rises with the raising of roasting temperature under 850°C. It should be noted that the height of the characteristic peaks of zinc oxide in Fig.2C is lower than Fig.2B, which may be caused by the evaporation of zinc oxide in 900°C. Confirmed by the results of XRD analysis, the zinc ferrite in zinc calcined is well decomposed into zinc oxide and magnetite and the optimal roasting temperature is 850°C.


A
intensity(counts)
2 θ
ZnFe2O4
Fe3O4
PbS
Zn2SiO4


B
intensity(counts)
2 θ
ZnFe2O4
Fe3O4
ZnO
Zn2SiO4

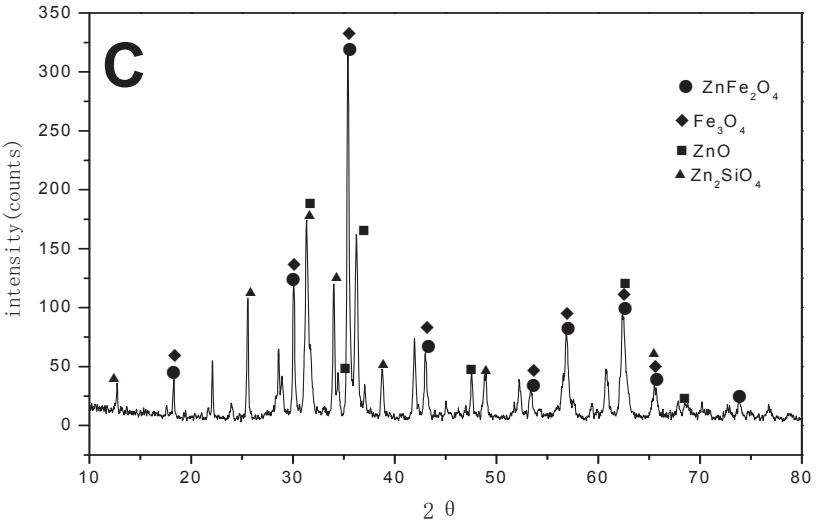


Figure 2 XRD of roasting product roasted at A: 700°C, B: 850°C and C: 900°C

3.2 Effect of roasting temperature on the distribution of zinc and iron

The effect of roasting temperature on the distribution of zinc and iron at varied particle size was investigated and the results were showed in Fig.3 and Fig.4. The distribution of zinc and iron at different particle size of roasting product roasted at 700°C, 850°C and 900°C. It is obvious that the maximum of zinc and iron distribution accrued at the particle size ranging from 48 μ m to 75 μ m. Also, for zinc, it can be seen from the comparison of Fig.3A-C that the value of the maximum distribution has greater variation which declined from 45.6% under 700°C to 37.68% under 850°C and then rise to 45.9% under 900°C; for iron, as was shown in Fig.4, the value of the maximum distribution decreased from 45.8% under 700°C to 38.4% under 850°C and then increased to 49.4% under 900°C. The regulation of iron distribution is similar to zinc and the reasonable interpretation might be given as follows: the decomposition of zinc ferrite and the generation of zinc oxide under 850°C caused the declining of particle size, and the proportion of zinc and iron distribution between 48 μ m to 75 μ m also decreased comparing to 700°C, while the sample particles was melted under 900°C. Consequently, the particles sintered with each other tightly, which caused the increase of particle size and the maximum distribution rose to 45.9% under 900°C.

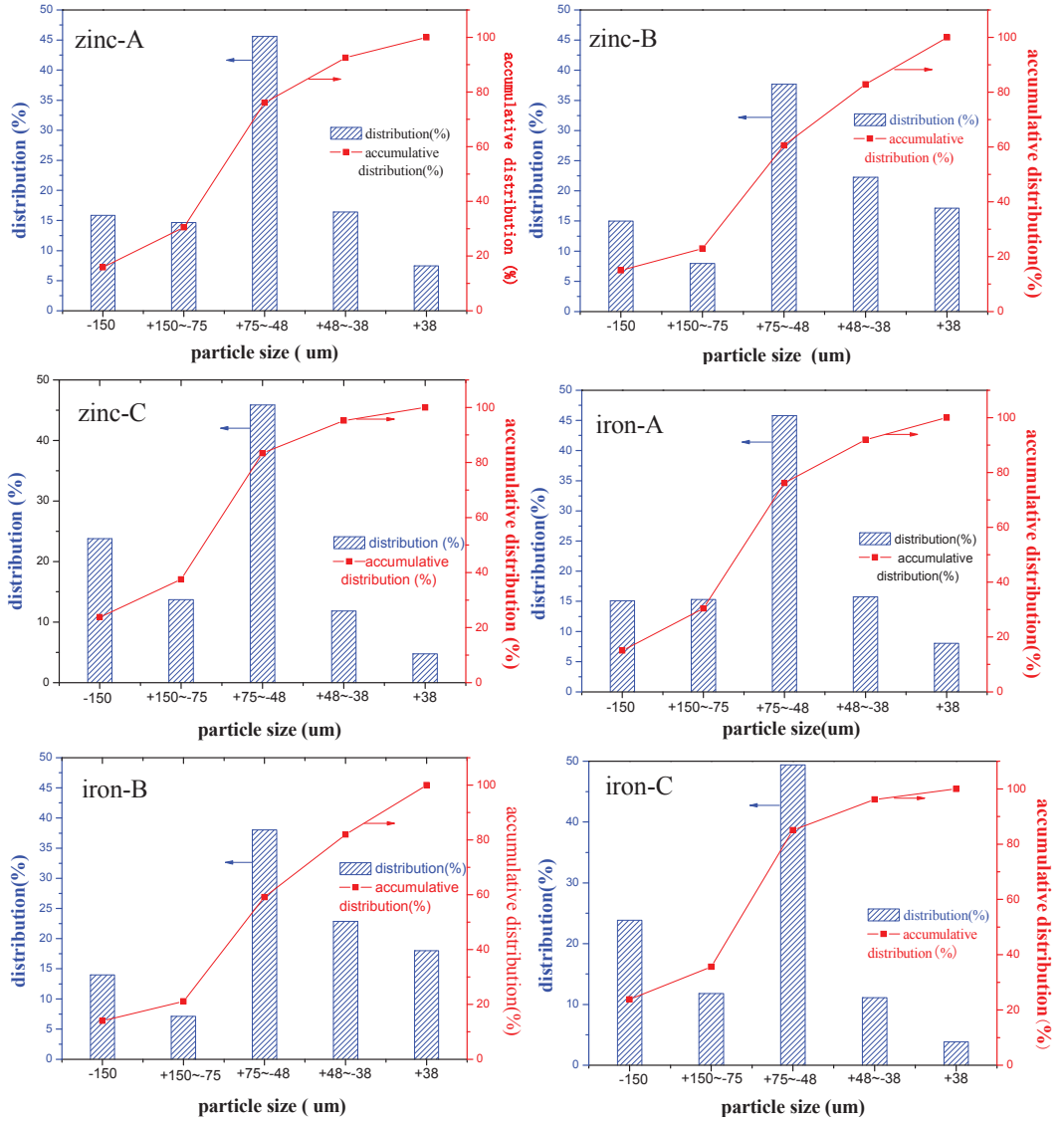


Figure 3particle size distribution of zinc and ironin roasting product roasted at A: 700°C, B: 850°C and C: 900°C

3.3 Effect of roasting conditions on the zinc and ironextraction

3.3.1 Effect of roasting temperature on the zinc and iron extraction

The effect of roasting temperature on extraction of zinc and iron was studied at different roasting temperature (700°C-900°C). Fig.5 shows that the reaction temperature has obvious effect on the leaching process under experimental conditions. Iron extraction (Fig.5A) reaches itsmaximum (28.00%) at 800°C

and then decreases to its minimum (11.20%) at 900°C, and this value is lower than the iron extraction of original zinc leaching residue. The extraction of zinc (as was shown in Fig.5B) has its maximum (75.5%) at 850°C and decreases greatly with the increase of roasting temperature. Combined by the result of the extraction of zinc and iron, the optimal roasting temperature for the decomposition of zinc ferrite is determined as 850°C.

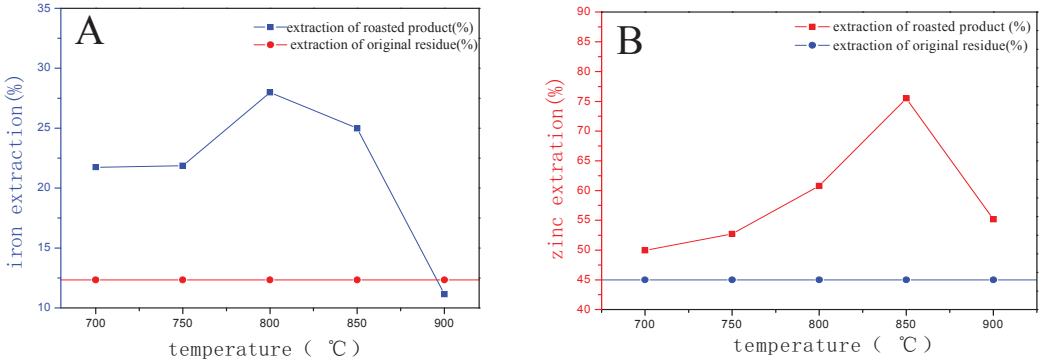


Figure 4. Effect of roasting temperature on the extraction of A: iron and B: zinc

3.3.2 Effect of roasting time on the zinc extraction

The effect of reaction temperature on the percentage of extracted zinc and iron at different reaction times is plotted in Fig. 6. It is observed that the extraction of iron and zinc increases with the extension to roasting time and both of them reach the maximum at 3h. It is interesting to note that the iron extraction increases suddenly (from 25.0% to 50.7%) at the roasting time of 2h, which may be caused by the over-reduction of iron and the generation of Fe(Ⅱ). As is described in INTRODUCTION, the high extraction of iron will bring lengthy purification process before electro win of zinc solution; this process consumes large quantity of manpower and materials and pollutes the environment as it could produce huge numbers of iron slag.Though the extraction of zinc is as high as 85.1% when the roasting time is 3h, the iron extraction is 62.7%, which is so high that this roasting condition is unsuitable for mass production. To have a high zinc extraction and low iron extraction, the optimal roasting time is 2h, at which the extraction of zinc and iron are kept at 75.5% and 25.0% respectively.

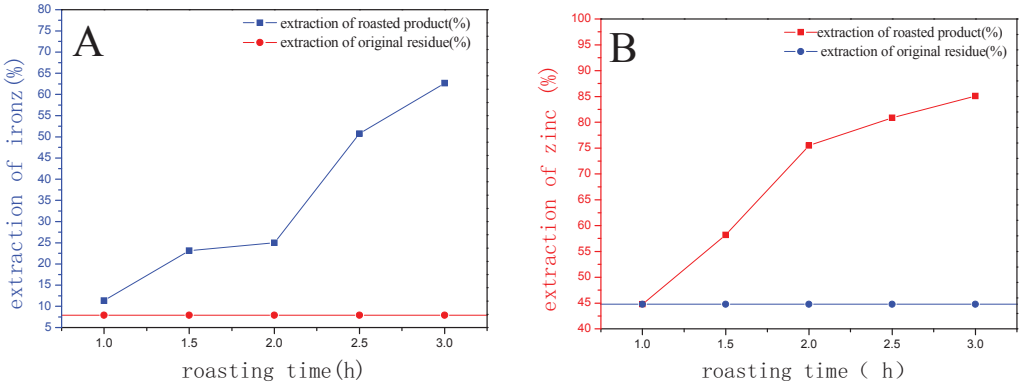


Figure 5.Effect of roasting time on the extraction of A: iron and B: zinc

4. Conclusions

1) The results of XRD showed that zinc ferrite was well decomposed to form zinc oxide and magnetite in the presence of a reducing gas mixture.

2) The roasting temperature has a slight effect on the distribution of zinc and iron at different particle size. The rule of the distribution of both zinc and iron are similar. Besides, changing their distribution is mainly caused by the decomposition of zinc ferrite (decreasing of particle size) below 850°C and the self-sintering (increasing of particle size) at temperature over 850°C.

3) The effect of roasting conditions on the decomposition of zinc ferrite is also evaluated by the extraction of zinc and iron in acid leaching process. The result of temperature experiment shows that the extraction of iron and zinc reach their maximum at 800°C and 850°C, and the roasting time experiment shows that the maximum of iron and zinc extraction appeared at 3h.

4) To get low iron extraction and high zinc extraction, the optimal roasting conditions is 850°C, 2h.

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